complexation,[6,15] which could lead to a cancellation of effects.

The structure of the N-phenylporphyrin complex, Zn(N-PhTPP)Cl, shows that the phenyl ring is relatively unhindered and free to rotate as indicated from its NMR spectrum. The N-C(phenyl) bond distance of 1.491 Å indicates a strong bond, consistent with the finding that N-phenylporphyrins show an unusually high stability against removal of the N substituent.[12] The structure of the coordination site and the porphyrin ring topology are closely related to those of the corresponding N-methyl complex,[6c] suggesting that the metal-nitrogen bond lengths and the cant of the pyrrole rings may be determined principally by the metal ion rather than the nitrogen-bound substituent. The comparison of Zn(II) complexes, however, may be misleading since the Zn-NR bond distance is long.[6c] A comparison of structures involving metals that form a stronger M-NR bond (such as Fe(II)[6d] or Mn(II)[6b]) would establish this point. The differences in spectral properties between N-phenyl- and N-alkylporphyrins and their complexes appear to be due to electronic rather than structural differences.

Acknowledgment. We are grateful for support of the NIH (CA 25457) and the PSC-BHE grants program of the City University of New York. The Nicolet R3m/E X-ray diffractometer and computing system at Colorado State University was purchased with funds provided by the NSF (CHE 8103011). We thank A. Sudhakar with assistance in obtaining NMR spectra.

Registry No. N-PhH(TPP), 81856-91-9; N-CH_3H(TPP), 51552-53-5; N-CH_2CH_3H(TPP), 73568-09-9; N-($CH_2CO_2C_2H_5$)H(TPP), 53226-50-9; N-(p-$CH_2C_6H_4NO_2$)H(TPP), 80641-51-6; Zn(N-Ph(TPP))Cl, 84079-98-1; Zn(N-CH_3(TPP))Cl, 59765-81-0; Fe(N-Ph(TPP))Cl, 83219-61-8; Fe(N-CH_3(TPP))Cl, 64813-94-1; Fe(N-C_2H_5(TPP))Cl, 88376-67-4.

Supplementary Material Available: Table I, listing atomic coordinates and U_{iso} for non-hydrogen atoms of Zn(N-Ph(TPP))Cl (1 page). Ordering information is given on any current masthead page.

Oxygen-17 NMR and Oxygen-18-Induced Isotopic Shifts in Carbon-13 NMR for the Elucidation of a Controversial Reaction Mechanism in Carbohydrate Chemistry

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The formation of 1,4-anhydro-6-azido-2,3-di-O-benzoyl-6-deoxy-β-D-galactopyranose (**3a**) from 1-O-acetyl-2,3-di-O-benzoyl-4,6-bis-O-(methylsulfonyl)-α-D-glucopyranose (**1b**) by treatment with sodium azide was suggested to proceed by way of a ring contraction process (Figure 1, pathway a).[1] Subsequently, an alternative mechanism was proposed, pathway b, for the formation of **3a** and closely related 1,4-anhydro sugars.[2] According to pathway b, the reaction is initiated by attack at the acetyl carbonyl atom followed by anomerization of the derived C-1 oxy anion **2**, which then displaces the methylsulfonyl group from C-4 (Figure 1).[2] In the case of pathway b, C-4 becomes attached to the anomeric oxygen atom O-1 while the contraction procedure shown in pathway a requires C-4 to be bonded to the ring oxygen atom O-5. In order to elucidate the mechanism of this reaction, Ferrier suggested the necessity for its reinvestigation.[3] With the help of oxygen-17 NMR spectroscopy[4] and oxygen-18-induced isotopic shifts in carbon-13 NMR,[5] we present evidence here for the mechanism of the formation of the trisubstituted 2,7-dioxanorbornane structure **3a** according to pathway b. The techniques used appear to be the first structural applications to carbohydrate chemistry.

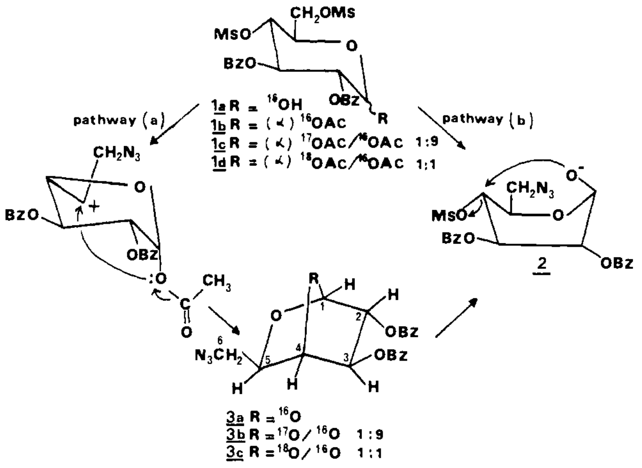

Figure 1.

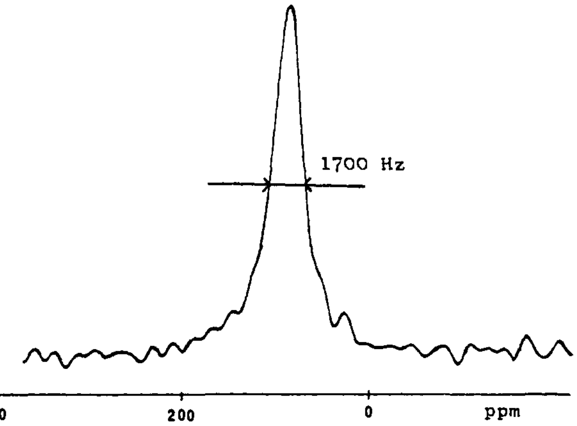

Figure 2. ^{17}O NMR spectrum of 1,4-anhydro-6-azido-2,3-di-O-benzoyl-6-deoxy-β-D-galactopyranose-1,4-^{17}O (**3b**) (about 10% enrichment), measured at 53.6 °C, at 48.8 MHz on a WH-360 Bruker spectrometer on a 27-mg sample in 1.5 mL of $CHCl_3$. The chemical shift of the labeled oxygen atom is 85.9 ppm relative to external 1,4-dioxane with an estimated error of ±0.5 ppm. The natural abundance ^{17}O signals are not observed. T_{acq} = 2 ms, NS = 200 000, line width at half-height = 1700 Hz. Neither field frequency lock nor Guassian resolution enhancement was used.

Oxygen-17 NMR spectroscopy has found only very limited applications in organic chemistry as a result of the low natural abundance (0.037%) and sensitivity of this isotope ($I = {}^5/_2$).[4] Difficulties are also associated with an appreciable electric quadrupole moment of ^{17}O ($Q = -2.6 \times 10^{-26}$ cm^2) and large field gradients, inducing broad lines in medium-sized organic molecules. In spite of these problems the ^{17}O NMR chemical shifts of a number of monosaccharide derivatives were recently assigned from specifically labeled[6] and even from natural abundance samples.[7] The O-5 ether oxygen NMR signal of the hexopyranoses or hexopyranosides studied in the chair conformation

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was found between 48 and 66 ppm relative to external 1,4-dioxane.[6,7] In natural abundance studies the resonance of the ring oxygen appeared considerably broader than that of the other lines[7] as a result of the more restricted rotational freedom of O-5. From another work the surprisingly low-field oxygen NMR signal at 86.0 ppm of 7-oxanorbornane was also avaialble.[8]

This prompted us to label the anomeric oxygen atom[5b] of **1a** ($H_2{}^{17}O$ 10% enrichment, in boiling dry 1,4-dioxane) and after acetylation to treat **1c** with sodium azide. The 48.8-MHz ^{17}O NMR spectrum of the resulting purified 1,4-anhydro sugar **3b**, shown in Figure 2, indicates a very broad signal at 85.9 ppm in perfect agreement with that reported for 7-oxanorbornane[8] and strongly deshielded with respect to the ring oxygen atom of monosaccharides.[6,7] This result afforded evidence for pathway b in the formation of the 1,4-anhydro sugar **3b**.

However, neither the ^{17}O chemical shift of the model 2-oxanorbornane nor the signal position of O-5 of monosaccharides in conformations other than chair was available to us. Thus, it appeared advisable to prove that the ^{17}O NMR consistency of **3b** with 7-oxanorbornane was not fortuitous.

Therefore, labeling of the anomeric oxygen atom of **1a** was also carried out with 50% enriched $H_2{}^{18}O$. After acetylation and sodium azide treatment of **1d**, the resulting 1,4-anhydro sugar **3c** was examined by 100.62-MHz ^{13}C NMR spectroscopy. After Gaussian resolution enhancement,[9] oxygen-18-induced upfield isotopic shifts[5a,5b] of 0.025 ppm were detected at the two directly attached carbon sites (99.1 and 81.9 ppm in $CDCl_3$), assigned unambiguously by specific proton decoupling[1] to C-1 and to C-4, respectively. These resonances appeared as a pair of signals corresponding to the $^{13}C–^{16}O$ and $^{13}C–^{18}O$ species. This experiment confirmed the C-1 oxy anion mechanism of pathway b in the formation of the 1,4-anhydro sugar **3c**.

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Characterization of the First Examples of Isolable Molecular Hydrogen Complexes, $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W; R = Cy, *i*-Pr). Evidence for a Side-on Bonded H_2 Ligand

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We wish to report the first examples of isolable[1] transition-metal complexes containing a coordinated dihydrogen molecule, characterized by a variety of spectroscopic and structural methods to possess η^2-bonded H_2.

Toluene solutions of deep purple $M(CO)_3(PCy_3)_2$ (M = Mo, W)[2] react readily and cleanly with hydrogen (1 atm) precipitating yellow crystals of *mer-trans*-$M(CO)_3(PCy_3)_2(H_2)$ in 85–95% yields.[2,3] The tungsten P-*i*-Pr_3 analogue is isolated in lower yields from hexane, since it is very soluble in hydrocarbon solvents. $Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ could not be obtained as a solid although reversible color changes (purple ↔ yellow) in solution indicate H_2 addition. In all complexes the H_2 is extremely labile, and storage and handling under an H_2-enriched atmosphere is necessary. Immediate discoloration occurs upon exposure of microcrystalline samples to vacuum or argon, but the original color is instantly restored upon contact with H_2. Bulk loss of H_2 from the solids is slow at 20 °C ($P_{dissoc} \cong$ 10 torr for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ and 1 torr for the PCy_3 analogue), but the H_2 can be rapidly quantitatively removed from toluene solutions to give $M(CO)_3(PR_3)_2$ by flushing with argon or exposure to partial vacuum at 25–50 °C.

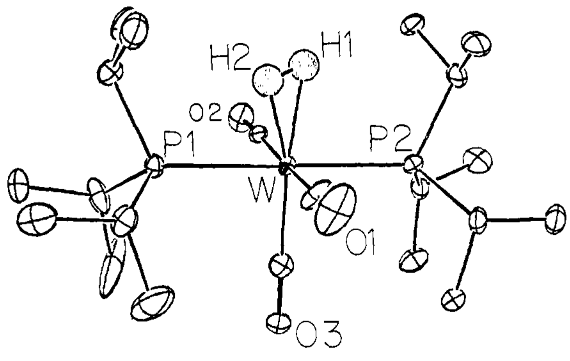

Figure 1. Geometry of the $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$ molecule with hydrogen atoms of the P-*i*-Pr_3 groups omitted for clarity. The positions of the two hydrogen atoms shown were derived from neutron data while heavy-atom positions are from −100(5) °C X-ray data.

Suitable single crystals of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ have been subjected to X-ray and neutron diffraction analyses. Because neutron diffraction is the method of choice for locating hydrogen atoms bound to heavy metals,[4] room-temperature neutron data were collected at the Los Alamos Pulsed Neutron Source utilizing the Laue time-of-flight method and were used to produce a difference–Fourier map phased on the non-hydrogen atom coordinates from room temperature X-ray studies.[5] This route clearly demonstrated the presence of both atoms of the H_2 ligand. Location of some other hydrogen atoms in the molecule was hampered by disorder in the phosphine ligands. Attempts to obtain detailed molecular parameters by least-squares refinement were ultimately hindered by this inability to properly model the phosphine ligands.

Subsequent low-temperature [−100 (5) °C] X-ray diffraction analysis[6] confirmed the location of the molecular hydrogen ligand.[9] Refinement in this case proved more tractable, since X-ray data are less sensitive to disorder involving phosphine hydrogen atoms. The resulting geometry about the tungsten atom (Figure 1) is that of a regular octahedron with "cis" interligand angles about tungsten ranging from 88.0 (4)° to 92.0 (6)°. The dihydrogen ligand is symmetrically coordinated in an η^2 mode with average tungsten–hydrogen distances of 1.95 (23) Å (X-ray) and 1.75 Å (neutron, ΔF). The H–H separation is 0.75 (16) Å (X-ray) and

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(6) $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ crystallizes in the centrosymmetric orthorhombic space group *Pcab* (No. 61) with a = 15.749 (3) Å, b = 24.219 (5) Å, c = 13.333 (3) Å, V = 5085.7 Å^3, and ρ_{calcd} = 1.54 g cm^{-3} for Z = 8 and M_r = 589.8. Automated diffraction data were collected at −100 (5) °C; the residuals for 2118 absorption corrected data [$2\theta_{max} = 45°$; $I > 2(\sigma)I$] are R_F = 4.3% and R_{wF} = 5.9%. All heavy atoms in the molecule were located and refined; hydrogen atoms of the P-*i*-Pr_3 groups were included in fixed positions. Weights were derived from standard counting statistics modified by an "ignorance" factor of 0.015. Calculations were performed on a CDC 7600 computer with use of local crystallographic programs developed by Dr. A. C. Larson.[7] Neutral atom scattering factors, modified by anomalous dispersion (except hydrogen), were used.[8]

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